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Extrapolation procedure in computation of dipole moment of polar liquid in nonpolar solvent

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There are several extrapolation procedures on ϵ_{012}, d_{12} and n_{012}^2 to compute the dipole moment μ of polar liquid dissolved in nonpolar solvent. As the solutions are usually made up by weights (Smith 1960) and easy to determine ω_2 than the concentration of solutes in moles per cc, the simplest form in which to express the concentration is the weight fraction ω_2 of the solute and the best one is to represent ϵ_{012} and n_{012} as a function of ω_2 by

$$\epsilon_{012} = a_0 + a_1\omega_2 + a_2\omega_2^2 \quad \ldots (1)$$

$$n_{012} = b_0 + b_1\omega_2 + b_2\omega_2^2 \quad \ldots (2)$$

where a's and b's are constants, ϵ_{012} and n_{012} are the dielectric constant and refractive index of solution of weight fraction ω_2 of the solute.

When,

$$\omega_2 \to 0,\ \epsilon_{01} = a_0,\ n_{01} = b_0,\ \left(\frac{\partial \epsilon_{012}}{\partial \omega_2}\right)_{\omega_2 \to 0} = a_1 \text{ and } \left(\frac{\partial n_{012}}{\partial \omega_2}\right)_{\omega_2 \to 0} = b_1$$

i.e. a_0, b_0, a_1 and b_1 are the extrapolated values of the dielectric constant and refractive index of the solution and slopes of variation of ϵ_{012} and n_{012} against ω_2 respectively at infinite dilution.

Guggenheim (1949, 1951) presented a formula to calculate μ of polar liquid in nonpolar solvents. Based on this formula Le-Fevre (1950) and Guggenheim (1951) applied different extrapolation techniques i.e. the ratio of finite difference on ϵ_{012} and n_{012}^2 against ω_2 to compute μ in case of triethylamine in benzene at 25°C and obtained different values i.e. 0·91 and 0·87 Debye respectively. This point made us interested to recalculate μ of that system from the more mathematical standpoint as stated above, and the calculated value of μ is found to be 0·864 Debye (when $\epsilon_{01} = n_{01}^2$) slightly lower than the expected value. By applying a correction term based on $\epsilon_{01} \neq n_{01}^2$, the μ agrees with the Guggenheim's value. In order to check the applicability of our extrapolation procedure, we have calculated μ of other five systems and are shown in Table 1.

The dielectric constant and the refractive index of a solution can be represented by Debye equation (1929),

Table 1. Values of a_0, a_1, b_0, b_1, $\mu_{cal.}$ and $\mu_{expt.}$

No.	Systems	Temp. in °C	a_0	a_1	b_0	b_1	μ (Debye)	μ (Debye)
1.	Triethylamine in benzene[1]	25	2·3053	0·42216	1·5004	−0·13051	0·87	0·87
2.	Aniline in benzene[2]	25	2·2702	3·12187	1·4981	0·08496	1·57	1·50–1·60
3.	Methylaniline in benzene[3]	25	2·2730	2·99060	1·4983	0·06774	1·65	1·64
4.	Dimethylaniline in benzene[4]	25	2·2730	2·51390	1·4981	0·07934	1·59	1·58
5.	Phenol in benzene[5]	22	2·2799	3·31870	1·4997	0·04727	1·64	1·62
6.	Diethylether in cyclohexane[6]	20	2·0311	1·96620	1·4259	−0·06245	1·35	1·29

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$$\frac{\epsilon_{012}-n_{012}^2}{(\epsilon_{012}+2)(n_{012}^2+2)} = \frac{4\pi N\mu^2}{27M_2kT}\,\omega_2, \qquad \ldots (3)$$

where N, d_{12}, M_2 and T are Avogadro number, density of the solution, molecular weight of the solute and temperature in 0°K respectively. Eq. (3) on differentiation with respect to ω_2 yields when $\omega_2 \to 0$ and $d_{12} \to d_1$

$$\mu^2 = \frac{27kT}{4\pi N}\cdot\frac{M_2}{d_1}\cdot\frac{1}{(\epsilon_{01}+2)^2}\left[\left(\frac{\partial\epsilon_{012}}{\partial\omega_2}\right)_{\omega_2\to 0} - 2n_{01}\left(\frac{\partial n_{012}}{\partial\omega_2}\right)_{\omega_2\to 0}\left(\frac{\epsilon_{01}+2}{n_{01}^2+2}\right)^2\right] \ldots (4)$$

when $\epsilon_{01} = n_{01}^2$, eq. (4) can be converted into a well known Guggenheim formula as shown by Jayprakash (1975). Now eq. (4) can be written in terms of the extrapolated values

$$\mu^2 = \frac{27kT}{4\pi N}\cdot\frac{M_2}{d_1}\cdot\frac{1}{(a_0+2)^2}\left[a_1 - 2b_0b_1\left(\frac{a_0+2}{b_0^2+2}\right)^2\right]. \qquad \ldots (5)$$

The values of a_0, b_0, a_1 and b_1 have been calculated from eqs. (1) and (2) against different systems by the usual least square method and the corresponding values of μ calculated from eq. (5) are finally placed in Table 1 with reported μ values.

In case of diethyl ether and phenol much reliance should not be given on compulation of dipole moment as the experimental values of the refractive indices of the solutions were not available. We, therefore, used the relation $n_{012} = x_1 n_{01} + x_2 n_{02}$ (Glasstone 1968) where x's and n's are the mole fraction and refractive indices of the pure solvent and solute respectively. The corresponding weight fraction of the solute ω_2 is related to x_2 by

$$\omega_2 = \frac{x_2 M_2}{x_1 M_1 + x_2 M_2}.$$

Since the determination of accurate dipole moment of polar liquid in non-polar solvent is difficult due to solvent though it is small (Smyth 1952) and other effects (Böttcher 1952) the problem should be attacked from the standpoint of polar molecular structure inorder to locate the more exactness in the value of μ. However, Table 1 shows a consistent calculated results of μ which are more or less equal to the reported ones. This proves the very soundness of the simple extrapolation technique which we have adopted in this note.

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